

Effect of spin-orbit coupling on magnetic and orbital order in MgV_2O_4

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Recent measurements on MgV_2O_4 single crystal have reignited the debate on the role of spin-orbit (SO) coupling in dictating the orbital order in Vanadium spinel systems. Density functional theory calculations were performed using the full-potential linearized augmented-plane-wave method within the local spin density approximation (LSDA), Coulomb correlated LSDA+U, and with SO interaction (LSDA+U+SO) to study the magnetic and orbital ordering in low temperature phase of MgV_2O_4 . It is observed that the spin-orbit coupling in the experimentally observed antiferromagnetic phase, affects the orbital order differently in alternate V-atom chains along c-axis. This observation is found to be consistent with the experimental prediction that the effect of spin-orbit coupling is intermediate between that in case of ZnV_2O_4 and MnV_2O_4 .

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I. INTRODUCTION

Vanadium spinels AV_2O_4 (A=Mg, Zn, Cd) are being studied extensively in recent years¹⁻⁶ as they provide a very interesting playground for the study of competing interactions on a frustrated lattice in 3-dimension. The Vanadium (V) ions at the B-sites of the spinel structure form a pyrochlore lattice, with corner sharing tetrahedra, which is geometrically frustrated. In its 3+ valence state, V ion has two electrons in the d-shell which, because of a strong Hund's coupling, align parallel to each other thereby imparting a high spin state ($S = 1$) to the ion. Thus in this family of spinels, there is a magnetic ion on a geometrically frustrated lattice resulting in competing ground states. Things get more involved when the partial occupancy of triply degenerate t_{2g} orbitals by the two d-electrons makes the orbital degree of freedom unfrozen. As both spin and orbital degrees of freedom remain active, there is a high possibility of spin-orbit (SO) coupling playing important role in the low energy physics of this family of systems. Role of this interaction has been a matter of debate recently^{1,3,4}. The manifestation of the interplay of orbital, spin and lattice degrees of freedom in these systems culminates in experiments as a sequence of phase transitions^{1,7,8}. A structural transition, often followed by magnetic transition as the temperature is lowered, signifies competing interactions trying to stabilize a particular ground state with gradual lifting of the frustration.

MgV_2O_4 , with a normal spinel structure, has been reported to undergo a structural transition at 51 K from cubic to tetragonal phase and a magnetic transition at 42 K from non-magnetic to an antiferromagnetic (AFM) phase consisting of alternating antiferromagnetic chains of V atoms running parallel to **a** and **b** directions as one goes along **c**-axis^{1,17}. The high temperature (HT) phase has a cubic spinel structure with $F\bar{4}3m$ symmetry where the V ion is surrounded by an almost perfect O_6 octahedron with all the six V-O bonds having same length. This leads to a sizable (~ 2.5 eV) $t_{2g} - e_g$ crystal field splitting of the d levels. There is of course a small trigonal distortion also present in this phase. Experimental results further reveal that the structural transition to the tetragonal phase at 51 K is accompanied by a compression along c-axis with $c/a=0.9941$. This lowers the symmetry to space group $I\bar{4}m2$. Hence, in addition to the $t_{2g} - e_g$ splitting arising from roughly O_6 octahedral coordination, a further splitting occurs due to the tetragonal compression where the low lying t_{2g} triplet splits into a lower energy singlet (d_{xy} orbital) and a higher energy doublet of d_{yz} and d_{zx} orbitals. The orbital degeneracy is thereby partially lifted with this structural distortion. Now out of the two d electrons, one goes to the lower energy d_{xy} orbital while the other still has a choice as it occupies the doubly degenerate d_{yz} and d_{zx} orbitals. This opens up a possibility of orbital order in this system. Structural transition also partially lifts the frustration of the V-V bonds in the pyrochlore lattice. This then brings in the second transition, at lower temperature of 42 K where a long range antiferromagnetic order sets in¹. Thus the presence of any orbital order and the magnetic order observed at low temperatures in all the Vanadium spinels are interrelated.

Several theoretical models have been proposed in the last few years to explain the possible orbital order in Vanadium spinels so as to be consistent with the observed antiferromagnetic order. Among these, the model proposed by Tsunetsugu and Motome³ is based on strong coupling Kugel-Khomskii Hamiltonian and predicts an orbital order where at each V site, d_{xy} orbital is occupied by one electron and the second electron occupies either d_{xz} or d_{yz} orbital, alternately, along the c-axis. However, this type of orbital order was found to be of lower symmetry than that ($I4_1/amd$) observed experimentally for ZnV_2O_4 . In an alternative theoretical model, Tchernychov⁴ considered a dominant SO interaction which then led to the proposal that the second electron would occupy a complex orbital of type $d_{xz} \pm id_{yz}$ at each V site. This orbital order is found to be consistent with the underlying crystal symmetry. Also it explains the low magnetic moment per V ion observed in these systems as a large negative orbital moment is expected from a strong SO coupling. These findings were also corroborated by electronic structure calculations⁵ for

ZnV₂O₄.

However, recent measurements on other members of the Vanadium spinel family raise doubts about the presence of a strong spin-orbit interaction effect. In fact, there has been a tremendous effort, from both theoreticians and experimentalists working on these systems, to bring out a unified picture in terms of the important interactions which underlie the two phase transitions (one structural and the other magnetic). In ZnV₂O₄ the SO coupling is found to be significant both from theory as well as experiments^{4,5,10} whereas in case of MnV₂O₄ there seems to be very little or no effect of the SO interaction on the orbital order^{11,12}. Recently Wheeler et al.¹ performed neutron diffraction measurements on MgV₂O₄ single crystal and speculated on the basis of their observations that MgV₂O₄ might come intermediate between ZnV₂O₄ and MnV₂O₄ as far as strength of SO coupling is concerned. Hence it is expected that in MgV₂O₄ the occupied orbitals, instead of being completely real (Tsunetsugu and Motome model) or completely complex (Tchernychov model), could be a mixture of real and complex orbitals. In the previous theoretical study on MgV₂O₄¹³, the issue of impact of SO coupling on orbital order has not been investigated. However, as stated above, SO coupling in MgV₂O₄ is expected to be non-negligible from experimental observations. In order to investigate thoroughly the effect of SO interaction on magnetic and orbital order in MgV₂O₄, we have carried out first principle electronic structure calculations incorporating SO coupling. Such a calculation is definitely expected to unfurl the strength of SO coupling in this system, the nature of orbital order (if there is any) and correlation of experimentally observed magnetic order with the orbital order, if present.

II. METHODOLOGY

We undertake an electronic structure calculation using full-potential linearized augmented-plane-wave method with the basis chosen to be linearized augmented plane waves as implemented in WIEN2K code¹⁴. The calculations have been carried out with no shape approximation to the potential and charge density. These calculations were performed at three levels of sophistication using local spin density approximation (LSDA), Coulomb correlated LSDA+U approximation, and with SO interaction i.e. LSDA+U+SO approximation. To remove the self-Coulomb and self-exchange-correlation energy included in LSDA approximation, we use self-interaction corrected scheme (LSDA+U(SIC))¹⁵, which is appropriate for the strongly correlated systems. The corrected energy functional is written as¹⁵

$$E = E^{LSDA} - [UN(N-1)/2 - JN(N-2)/4] + 1/2 \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + 1/2 \sum_{m \neq m', m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}$$

Here E^{LSDA} is the standard LSDA energy functional, U represents the on-site Coulomb interaction, J is the exchange parameter and $n_{m\sigma}$ are the occupations of the localized orbitals. N is the total number of localized electrons.

In the LSDA+U+SO calculations, SO coupling was considered within the scalar relativistic approximation and the second variational method was employed¹⁶. In this method, the eigen value problem is first solved separately for spin up and spin down states without inclusion of the SO interaction term (H_{SO}) in the total Hamiltonian. The resulting eigen values and eigen functions are then used to solve new eigen value problem with the H_{SO} term in the total Hamiltonian. This method is more efficient and computationally less expensive than the calculation in which H_{SO} is included in the total Hamiltonian by doubling the dimension of the original eigenvalue problem in order to calculate the non-zero matrix elements between spin-up and spin-down states. In this method, the calculation of H_{SO} matrix elements involves much less number of basis functions than in the original basis set.

MgV₂O₄ crystallizes in tetragonal structure with symmetry $I\bar{4}m2$ (space group 119) at low temperatures¹. Atomic positions and lattice constants were taken from the experimental data¹. The atomic sphere radii were chosen to be 1.96, 1.99, and 1.78 a.u. for Mg, V, and O, respectively. We have used 50 \mathbf{k} points in the irreducible part of the Brillouin zone for the self-consistent calculations. In order to model the low temperature magnetic order observed in the experiment, we have constructed a supercell (with 8 inequivalent Vanadium atoms). The lowering of symmetry of this unit cell arises due to the experimentally observed antiferromagnetic ordering. The network of corner sharing V₄O₄ cubes of low temperature structure is shown in Fig. 1 with the magnetic order. The 8 inequivalent Vanadium atoms considered in the calculation are also marked in the figure with the corresponding orientation of spins at that particular site. One can see the antiferromagnetic chains along **a** (...V3-V7-V3-V7...) and **b** (...V6-V2-V6-V2...) axes alternating along c-axis. In each V₄O₄ cube there are 4 inequivalent V atoms. Due to the presence of cooperative trigonal distortion along c-axis resulting in alternating compression and expansion of cube faces, there is a further symmetry breaking and hence successive cubes along c-axis no longer remain equivalent. Furthermore, the V₄O₄ cube containing V1, V5, V2 and V6 does not have the same spin arrangement as that containing V3, V7, V4 and V8. Therefore to model the experimentally observed magnetic order one needs to consider 8 inequivalent V atoms in the unit cell.

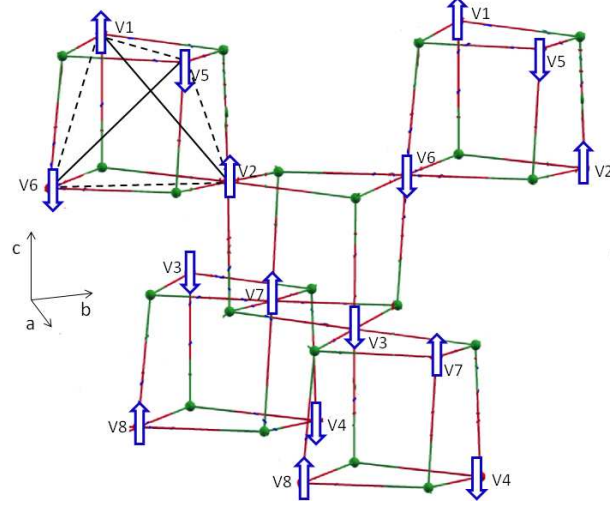


FIG. 1: Corner sharing network of V_4O_4 cubes in the low temperature structure of MgV_2O_4 showing the experimentally observed magnetic order. The solid and dotted lines joining the V atoms (shown in one cube) represent the shorter V-V FM bonds (2.971 Å) and longer V-V AFM bonds (2.98 Å) respectively.

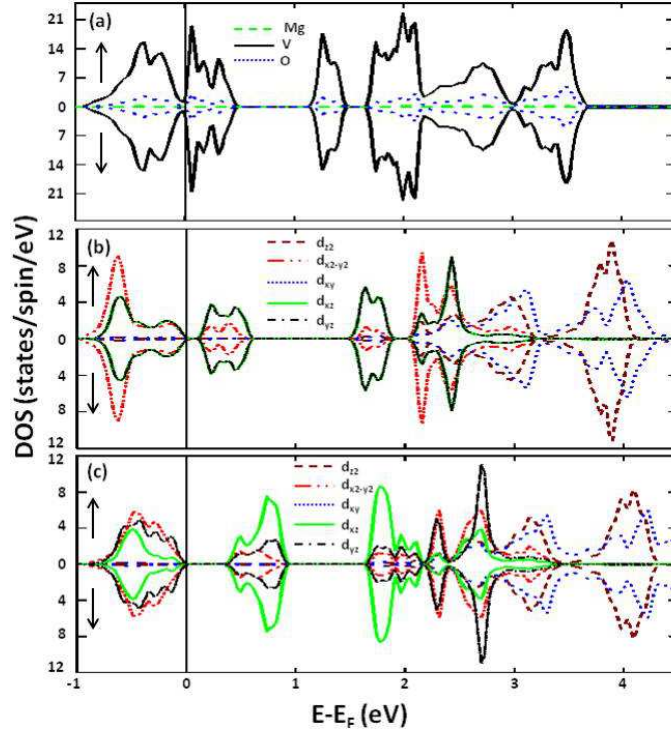


FIG. 2: Spin polarized (a) total DOS within LSDA, (b) partial DOS for V d-states around the Fermi level within LSDA+U, (c) partial d-DOS within LSDA+U+SO ($U-J = 2$ eV) in the low temperature AFM phase.

III. RESULTS

Our LSDA calculations of experimentally observed antiferromagnetically ordered phase show that total energy of this phase is indeed lower than that of the corresponding ferromagnetic (FM) phase by 0.4 eV per formula unit. The density of states (DOS) of this antiferromagnetic state (within LSDA) is shown in Fig. 2(a). It is observed that LSDA gives a metallic state whereas the system is known to be a Mott insulator¹⁷. Thus AFM interaction alone is not able to open up the gap. Around the Fermi level, mainly V d-states are seen to be present. In an effort to have the insulating gap as observed experimentally, we included Coulomb correlation in our calculations within LSDA+U approximation.

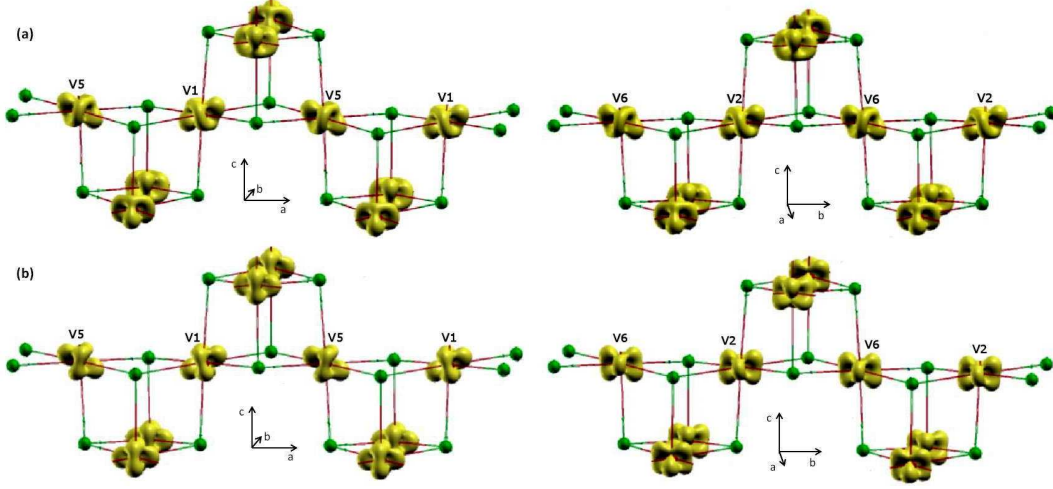


FIG. 3: Real space electron density at each V site within (a) LSDA+U (b) LSDA+U+SO along two different directions. Isosurface used for both corresponds to $0.5 \text{ e}/\text{\AA}^3$.

We performed calculations with U_{eff} ($=U-J$) values in the range 1 to 4 eV as found to be relevant from the literature on Vanadium spinel systems^{5,11,13}. We present the results for $U_{eff} = 2 \text{ eV}$ in the following, nevertheless it may be noted that our conclusions remain valid in the whole range of U_{eff} values considered by us. In Fig. 2(b) we show the partial DOS of five d-orbitals as these are the states present around the Fermi level. As expected, the application of Coulomb correlation U is able to open up a small gap of 0.12 eV which increases with the increase in U . The gap originates because of the splitting of the t_{2g} levels in addition to the $t_{2g}-e_g$ splitting due to octahedral field. The further splitting of t_{2g} is primarily caused by the antiferromagnetic interactions which get enhanced in the presence of Coulomb correlations.

Another observation that can clearly be made from the partial DOS of d-orbitals (Fig. 2(b)) is that among the occupied t_{2g} orbitals, one orbital (i.e. $d_{x^2-y^2}$) is more populated while the other two (d_{xz} and d_{yz}) essentially have the same occupancy and seem to be degenerate. The higher occupancy of $d_{x^2-y^2}$ orbital is a result of the presence of the tetragonal compression along c-axis at low temperatures. However, closer analysis of occupancies of the apparently degenerate d_{xz} and d_{yz} orbitals at each Vanadium site shows that there is a tendency towards orbital ordering. Table I lists the orbital occupancies of $d_{x^2-y^2}$, d_{xz} and d_{yz} for the 8 inequivalent V atoms in the unit cell considered. One clearly observes that the occupancy of d_{xz} and d_{yz} orbitals are different as one moves along the c-axis whereas that of $d_{x^2-y^2}$ remains the same. The orbital polarization increases on increasing the value of U and alternates for the d_{xz} and d_{yz} orbitals (see for example, V1 and V2) in successive Vanadium layers along c-axis. This is similar to an A-type antiferro-orbital order where the antiferromagnetic V chains parallel to the ab-plane have *ferro-orbital* order (e.g. similar orbital occupancies of V1 and V5 ions or that of V2 and V6 ions) whereas along c-axis there is an *antiferro-orbital* order between d_{xz} and d_{yz} orbitals (see occupancies of V1 and V2 or that of V5 and V6 in Table I). This is consistent with the previous theoretical observation on the same system¹³. The observed intra-chain ferro-orbital order is also consistent with experimental antiferromagnetic order as per Goodenough-Kanamori-Anderson rules¹⁸. The orbital order described above is also revealed in the calculated real space electron density at each V site shown in Fig. 3(a). This orbital order was predicted by Tsunetsugu and Motome³ for Vanadium spinels from their calculations based on Kugel- Khomskii model in strong coupling limit.

As mentioned earlier, the influence of spin-orbit coupling on the magnetic and orbital order in these systems is continuously debated but no conclusion has been reached yet. In order to investigate the effect of spin-orbit interaction in this particular system, we also performed a calculation with spin-orbit coupling within LSDA+U+SO approximation. The solution obtained within LSDA+U+SO has a lower energy than that obtained within LSDA+U by 0.095 eV per formula unit for $U_{eff}=2\text{eV}$. The partial DOS (Fig. 2(c)) clearly shows a non-negligible impact of SO in general, with an increased energy gap compared to that with LSDA+U.

The analysis of orbital occupancies in this case indeed leads to some important and interesting observations. The apparent degeneracy of d_{xz} and d_{yz} orbitals observed within LSDA+U is no longer present and there is a complete lifting of degeneracy of all the t_{2g} orbitals (see Table I). Even though, likewise LSDA+U, the antiferromagnetic V chains parallel to the ab-plane are still ferro-orbitally ordered and along c-axis these chains are anti-ferro orbitally ordered, the orbital polarizations in adjacent chains along c-axes are significantly different in the presence of SO interaction. For example, if we compare the occupancies (Table I) for V1 and V2 with LSDA+U and LSDA+U+SO,

TABLE I: Orbital occupancies and spin magnetic moment within LSDA+U and LSDA+U+SO ($U_{eff}=2$ eV)

	orbital occupation			spin magnetic moment (μ_B)
	$d_{x^2-y^2}$	d_{xz}	d_{yz}	
With LSDA+U				
V1 (V3)	0.665	0.553	0.386	1.53 (-1.53)
V2 (V4)	0.665	0.386	0.553	1.53 (-1.53)
V5 (V7)	0.665	0.553	0.386	-1.53 (1.53)
V6 (V8)	0.665	0.386	0.553	-1.53 (1.53)
With LSDA+U+SO				
V1 (V3)	0.595	0.451	0.591	1.574 (-1.574)
V2 (V4)	0.759	0.214	0.665	1.571 (-1.571)
V5 (V7)	0.595	0.451	0.591	-1.574 (1.574)
V6 (V8)	0.759	0.214	0.665	-1.571 (1.571)

TABLE II: Calculated orbital moments, total magnetic moment (J) (in μ_B) and angle of J w.r.t. z-axis within LSDA+U+SO ($U_{eff} = 2$ eV). The spin magnetic moment is along z axis and is listed in Table I

	$\mu_{orbital}$			μ_{total} J	angle
	x	y	z		
V1	-0.355	0.000	-0.466	1.15	17.79
V2	-0.015	-0.030	-0.510	1.05	1.90
V5	-0.355	0.000	0.466	-1.15	162.21
V6	-0.015	-0.030	0.510	-1.05	178.10

we note that orbital occupancies of $d_{x^2-y^2}$ are no longer same in presence of SO interaction. Furthermore, the polarization of the d_{xz} and d_{yz} orbitals are also very different (i.e. at V2 the polarization of d_{yz} orbital w.r.t. d_{xz} is much stronger than that at V1). This implies that V chains in successive layers along c-axis are affected differently by the SO interaction. This is also reflected in the orbital moments of V ions (listed in Table II and depicted in Fig. 4). The calculated electronic density at each V site is shown in Fig. 3(b) which brings out the impact of SO interaction.

In Fig. 4 we show two successive Vanadium chains along c-axis with the calculated electron density at each Vanadium site in the presence of both Coulomb correlation and SO interaction. We have also marked the direction of orbital and magnetic moments at each site. Effect of SO interaction is clearly different on the two chains and so is the arrangement of the orbital moments. One chain shows the canted orbital arrangement and orbital moments are making an angle of 17.79° with the c-axis whereas in other chain orbital moment makes an angle of 1.90° (almost collinear orbital arrangement) with the c-axis (Table II). On one chain (V1-V5-V1-V5) due to canting of orbital

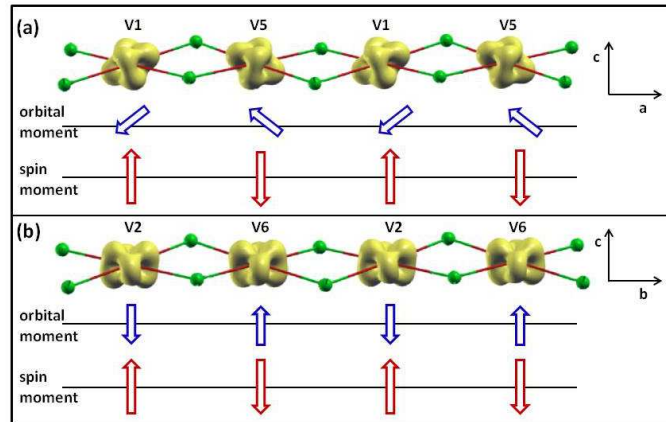


FIG. 4: Electron densities for two successive Vanadium chains along c-axis within LSDA+U+SO showing the impact of SO interaction on them. The directions of corresponding orbital and magnetic moments are also shown below each chain.

moment, the effect of SO interaction reduces whereas in the other chain orbital moments align almost opposite to the magnetic moment implying a substantial SO interaction. The observation that the SO interaction appears to affect alternate V chains along c-axis differently, is interesting. This also substantiates the speculation of Wheeler et al.¹ that SO interaction in MgV_2O_4 may not be as large as that in ZnV_2O_4 or as small as that in MnV_2O_4 as discussed earlier. The magnitude of orbital moments observed in our calculation also corroborates this fact. Thus our results show that a small but non-negligible spin-orbit coupling, along with the significant trigonal distortion present in MgV_2O_4 structure, has a substantial effect on the orbital order of this system. This observation is consistent with the experimental observations by Wheeler et al.¹ of antiferromagnetic chains with a strongly reduced moment and the one-dimensional behavior and a single band of excitations projected by the inelastic neutron scattering.

IV. CONCLUSIONS

To conclude, we have studied the effect of spin-orbit interaction on magnetic and orbital order in the low temperature tetragonal phase of MgV_2O_4 . We observe that even though the orbital moments are relatively small compared to those of ZnV_2O_4 , the orbital order in successive Vanadium chains is differently affected in the presence of SO interaction. In one chain (V1-V5-V1-V5, parallel to crystallographic **a** axis) the three t_{2g} orbitals are nearly equally populated giving rise to a canted (non-collinear) arrangement of orbital moments whereas in the other (V2-V6-V2-V6, parallel to **b** axis), the orbitals are highly polarized leading to a collinear arrangement of orbital moments. These results imply that SO interaction in MgV_2O_4 is non-negligible and has a significant effect on orbital order. However it is not very strong unlike ZnV_2O_4 and at the same time not very weak unlike MnV_2O_4 .

V. ACKNOWLEDGEMENT

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